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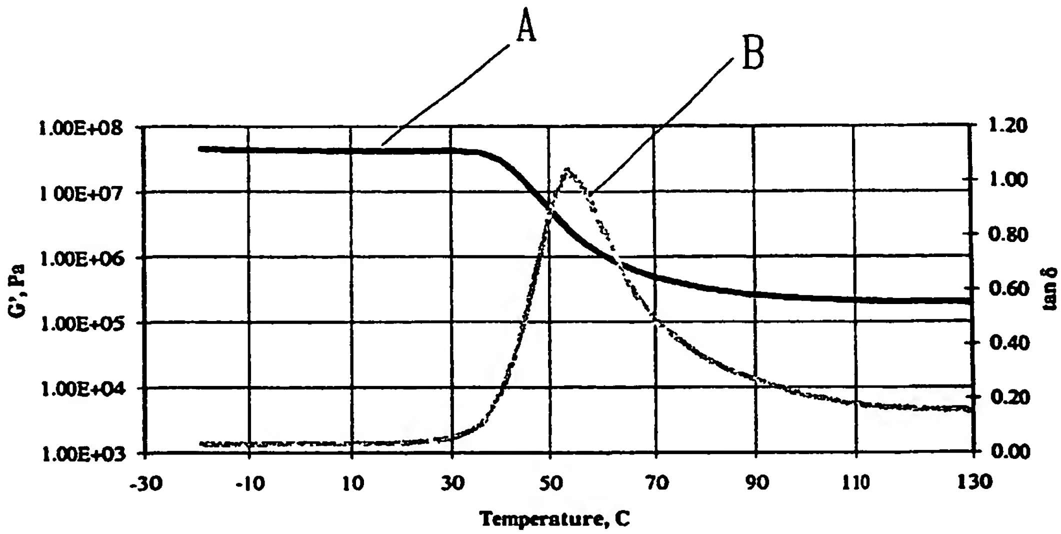
[Continued on next page]

(54) Title: PROCESS FOR COATING A WEB WITH A COATING POWDER



(57) Abstract: The present invention relates to a method for coating a surface of a web, with a dry coating powder. The coating powder comprises inorganic material and polymeric binder material. The polymeric binder material is selected in such a manner that when increasing the temperature above the glass transition temperature the ratio G''/G' is at the most equal to the ratio G''/G' in the glass transition temperature.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

PROCESS FOR COATING A WEB WITH A COATING POWDER

The present invention relates to a method for coating a surface of a web, which fibrous portion consist of papermaking fibres, with a coating powder comprising steps of:

- selecting raw materials of the coating powder comprising inorganic material and polymeric binder material, the polymeric binder material having a characteristic glass transition temperature T_g above which a rubbery state plateau exists, and a dynamic modulus, which consists of a measurable elastic component G' and a measurable loss component G",
- forming the coating powder from the raw materials,
- allowing the web to move between electrodes, which are in different potentials,
- applying the coating powder on the surface of the web by utilizing the difference in the electric potential, and
- finishing the coated surface of the web in a process step in which the process is arranged to achieve its maximum temperature, which exceeds the glass transition temperature T_g of the polymeric binder material.

A dry surface treatment process is a known method in which dry coating powder is applied on a web. The coating powder includes inorganic material and polymeric binder material. A problem related to coating by the dry surface treatment process is a behaviour of the polymeric binder material during the process. The viscoelastic properties of polymers depend on the temperature and frequency of deformation. On the one hand, the polymeric binder material should soften and form a film at least partially in a certain process conditions because otherwise the cohesion strength of the powder-formed layer and its adhesion to the web is insufficient. On the other hand, the softened polymeric binder material must not adhere to counter surfaces with which it is in contact during the process.

The method of the invention overcomes the above-mentioned problems. It is characterized in that the polymeric binder material is

selected in such a manner that when increasing the temperature above the glass transition temperature the ratio G"/G' is at the most equal to the ratio G"/G' in the glass transition temperature.

When the ratio G"/G' is at the most 1 in the rubbery plateau the polymeric binder material does not adhere to the counter surfaces during processing. Energy and costs can be saved in the process because polymeric binder materials having a low glass transition temperature (in other words, materials having a low softening temperature) can be used. Also shorter dwell times can be used in the process.

The present invention is utilized in a dry surface treatment process in which a web is allowed to move between electrodes, which are in different potentials. The coating powder is electrically charged by at least one electrode at one side of the web, and charged particles of the coating powder are applied on the surface of the web by utilizing an electric field, which is created between the electrode at the one side of the web and at least one electrode at the other side of the web. The potential difference between the electrodes can be created by electrodes having opposite polarities, or by an electrode being either positive or negative and a ground electrode. After a coating layer has been formed on the web the coated surface of the web is finished by using heat and pressure in such a manner that the polymeric binder material at least partially melts. In the finishing step the process achieves its maximum temperature.

The preferred ranges for the thermomechanical treatment are: The temperature of 80–350°C, the linear load of 25–450 kN/m and the dwell time of 0.1–100 ms (speed 150–2500 m/min; nip length 3–1000 mm; in one passage). The thermomechanical treatment can be made by various calendering methods or calendering-like methods. The methods utilize nips formed between rolls, or substantially long nips formed between two counter surfaces. Examples of such nips are hard-nip, soft-nip, long-nip (e.g. shoe-press or belt calender), Condebelt-type calender and super-calender.

The fibrous portion of the continuous web to be treated consists of papermaking fibres. In the present application, the papermaking fibres refer to fibres obtained from trees, in other words, either fibres of a mechanical or chemical pulp or mixtures of those two.

The coating powder includes inorganic particles (e.g. ground $CaCO_3$, precipitated $CaCO_3$, kaolin, talc, TiO_2 etc.) and polymeric binder particles. Suitable polymeric materials for polymeric binder particles are for example styrene-butadiene or acrylate copolymers. The polymeric binder material may comprise several polymers, and its characteristics may be modified. The inorganic particles and the polymeric binder particles can be separate particles, or an inorganic portion and a polymeric portion may be integrated into same particles. The average diameter of the material particles is usually 0.1 – 500 μm, preferably 1 – 15 μm.

The coating powder comprises 10.1 – 99.5 wt-% (dry weight) of inorganic material and the rest is preferably polymeric binder material. The coating powder comprises preferably at least 70 wt.-% of inorganic material and more preferably at least 80 wt.-% of inorganic material. The coating powder comprises preferably at the most 99 wt.-% of inorganic material and more preferably at the most 95 wt.-% of inorganic material.

For a known polymer composition that includes an amorphous phase, there is a known or characteristic range of temperatures where the glass transition takes place. This transition region, which with increasing temperature corresponds to a change in the mechanical properties of the material, is generally described as a change from glassy to rubbery state. The glass transition temperature, which can be taken characteristic for each type of polymers, but is affected e.g. by chemical means, is usually determined in a static state. Exerting a dynamic deformation into the material shifts the transition temperature towards higher temperatures.

The viscoelastic behaviour of a material determines a flowing ability of a material. Mechanical properties of viscoelastic material under dynamic loading can be denoted by the elastic and viscous components of the dynamic modulus, which for example in torsional deformation mode are the shear storage modulus G' and shear loss modulus G".

The ratio G"/G' is called a loss factor, which typically reaches its maximum in the glass transition temperature. Above the glass transition temperature there is a range called a rubbery state plateau. In the rubbery state plateau the loss factor changes less. Typically, the loss factor in the rubbery state plateau does not exceed a level, which is at the most 80 % from the level, which is reached in the glass transition temperature. In general a level corresponding to 50 % of the glass transition temperature level is not exceeded. For polymeric binder materials, which have a distinct melting point T_m, the rubbery state plateau can be defined as a range between the glass transition temperature and the melting point. For materials not having a distinct melting point, the rubbery state plateau can be defined simply as a rubbery state.

The finishing step in the thermomechanical treatment causes deformations in the coating layer. The deformation properties of the whole coating are affected by e.g. the binder selection and content, additives and interactions between the binder and the pigments. When the web is not loaded (e.g. compressed) any more, some of the deformations recover and some last (permanent change). The ratio G"/G' measured for the binder indicates the formation of permanent changes within the material under deformational stresses.

The properties of the properly selected polymeric binder material during the dry surface treatment process can be described as follows: When the elastic component G' of the dynamic modulus remains stable at high enough level and the ratio G"/G' is 1 at the most in the rubbery state plateau, the adhesion of the polymeric binder material to the counter surfaces during processing is diminished. In other words, the

elastic component G' shall be higher or at least equal to the loss component G" above the softening temperature of the polymeric binder material. The loss factor may be almost constant, or slightly increasing or decreasing. Preferably the loss factor is constant and maintains steady in range 0.2 – 1.0, or more preferably in range 0.2 – 0.6 when measured at elevated temperatures and conditions corresponding to the processing. The elastic modulus (the shear storage modulus) of the polymeric binder material is preferably at least 1.0×10^5 Pa when measured at fixed conditions corresponding the thermomechanical treatment. This high elasticity typically requires polymer crosslinking to a some degree. Hence, the polymeric binder material is selected in such manner that when increasing the temperature above the glass transition temperature the ratio G"/G' is at the most equal to the ratio G"/G' in the glass transition temperature. The glass transition temperature is determined in the same conditions as the loss factor. Preferably at measuring conditions corresponding to the dry surface treatment finishing step the ratio G"/G' is at the most 1 in the rubbery state plateau. More preferably the ratio G"/G' is at the most 1 between the glass transition temperature of the polymeric binder material and the maximum processing temperature (the temperature in the coating material).

The viscoelastic properties during a thermomechanical treatment can be determined according to ASTM D5279-01 in a following manner: An even film of 1 to 3 mm in thickness is manufactured from a polymeric binder material. The film is put under torsional stress, and at the same time the film is allowed to move through a specific temperature range. As the viscoelastic properties vary between measuring conditions, it is important to specify the conditions in each case. The used temperature range was –30 - 130°C and the temperature rise 3°C/min. The used frequency was 1 Hz. The torsional loading created shearing in the material with an adjusted strain of 16 % (in relation to a full circle).

In the following, the invention is explained by referring to figures in which

Figures 1 and 2 show curves representing an elastic modulus and a loss factor as a function of temperature.

In figure 1, the elastic component G' of the shear modulus is represented by a curve A, and the loss factor G"/G' is represented by a curve B. The curves show properties of a polymeric binder material, which has acceptable characteristics for use in the dry surface treatment process. The elastic modulus is at least $1{,}0 \times 10^5$ Pa, and the loss factor is at the most 1. The characteristic glass transition temperature of the material is 24°C (measured in the static state). However, a peak in the curve B representing the glass transition temperature has been shifted towards higher temperatures due to a dynamic measurement method.

In figure 2, the elastic component G' of the shear modulus is represented by a curve C, and the loss factor G"/G' is represented by a curve D. The curves show properties of a polymeric binder material, which has no acceptable characteristics for use in the dry surface treatment process. The elastic modulus is below $1{,}0 \times 10^5$ Pa when the temperature exceeds 75°C, and the loss factor is over 1 when the temperature exceeds 110°C. The characteristic glass transition temperature of the material is 24°C. It is very probable that this polymeric binder material disadvantageously sticks onto surfaces during processing.

The invention is not restricted to embodiments explained above but it may vary in the scope of the claims.

Claims:

1. A method for coating a surface of a web, which fibrous portion consist of papermaking fibres, with a coating powder comprising steps of:
- selecting raw materials of the coating powder comprising inorganic material and polymeric binder material, the polymeric binder material having a characteristic glass transition temperature T_g above which a rubbery state plateau exists, and a dynamic modulus, which consists of a measurable elastic component G' and a measurable loss component G",
- forming the coating powder from the raw materials,
- allowing the web to move between electrodes, which are in different potentials,
- applying the coating powder on the surface of the web by utilizing the difference in the electric potential, and
- finishing the coated surface of the web in a process step in which the process is arranged to achieve its maximum temperature, which exceeds the glass transition temperature T_g of the polymeric binder material,

characterized in that the polymeric binder material is selected in such a manner that when increasing the temperature above the glass transition temperature the ratio G"/G' is at the most equal to the ratio G"/G' in the glass transition temperature.

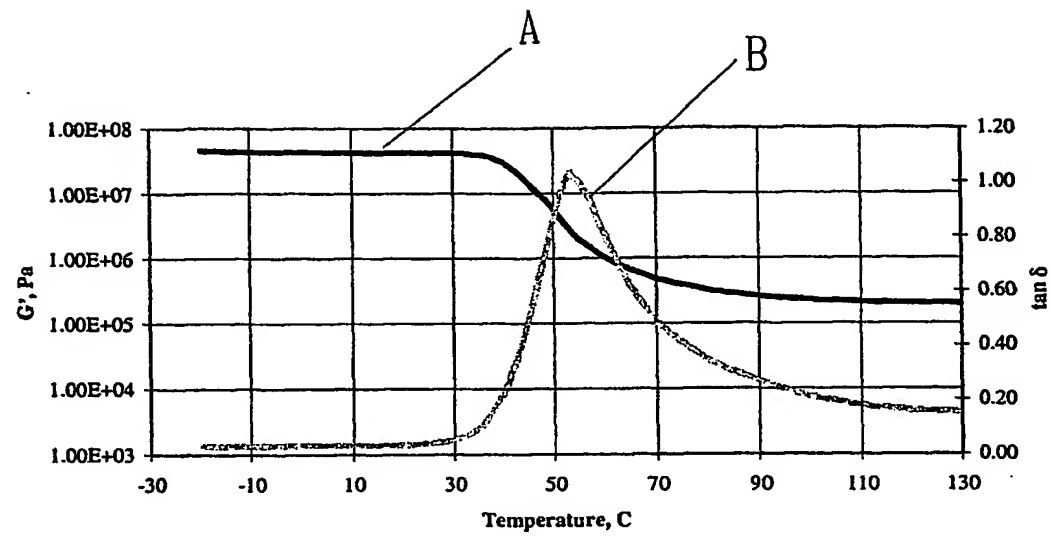
2. The method according to claim 1, **characterized** in that the ratio G"/G' is at the most 1 in the rubbery state plateau.

3. The method according to claim 1 or 2, **characterized** in that the ratio G"/G' is at the most 1 between the glass transition temperature and the maximum process temperature.

4. The method according to any preceding claim, **characterized** in that the elastic modulus is at least 1.0×10^5 Pa in a temperature range, which is below the maximum process temperature.

5. The method according to any preceding claim, **characterized** in that the loss factor in the rubbery state plateau is at the most 80 % of the value, which is reached in the glass transition temperature.

6. The method according to claim 5, **characterized** in that the loss factor in the rubbery state plateau is at the most 50 % of the value, which is reached in the glass transition temperature.


A
B
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1.00
0.80
0.60
0.40
0.20
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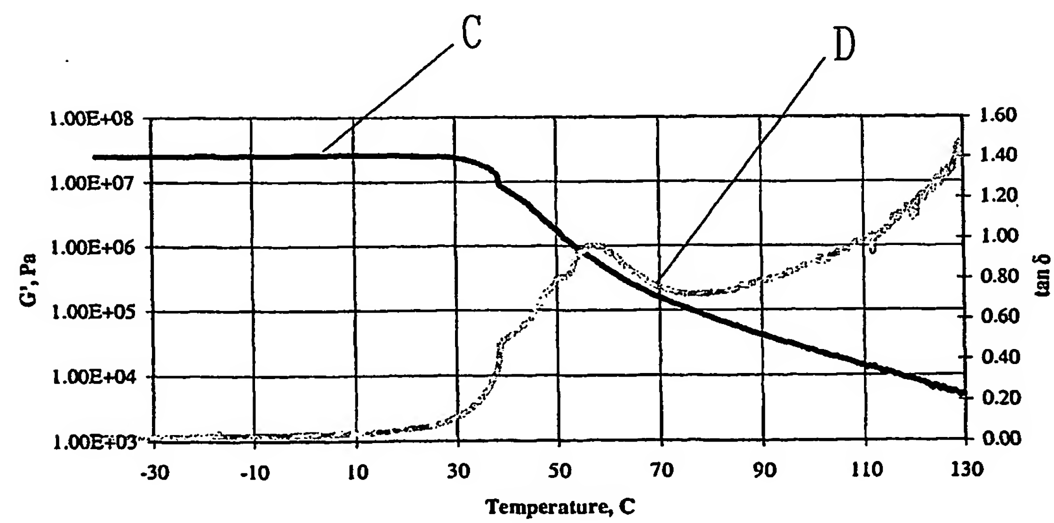
tan δ
-30
-10
10
30
50
70
90
110
130
Temperature, C

Fig. 1.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1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
tan δ
-30
-10
10
30
50
70
90
110
130
Temperature, C

Fig.2.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FI 03/00867

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21H19/00 B05D1/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21H B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAPERCHEM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 982 120 A (BANDO CHEMICAL IND) 1 March 2000 (2000-03-01) page 2, line 55 -page 3, line 12 page 4, line 27 -page 5, line 25	1-6
X	EP 0 958 865 A (BANDO CHEMICAL IND) 24 November 1999 (1999-11-24) page 4, line 45 - line 51 page 5, line 54 -page 6, line 36	1-6
X	WO 02 45869 A (MEINANDER KERSTIN ;KAERNAE TOIVO (FI); NYBERG TIMO R (FI); KAESMAE) 13 June 2002 (2002-06-13) page 3, line 12 -page 4, paragraph 25	1-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 April 2004	28 APR 2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	SUSANNA LINDFORS/ELY

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 03/00867

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: part of claims 1-6
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: part of claims 1-6

Present claims 1 - 6 relate to a method defined by reference to the following parameters:

When the temperature is increased above the glass transition temperature, the ratio G''/G' (the loss factor) is at the most equal to the ratio G''/G' in the glass transition temperature, wherein G' represents the elastic component and G'' represents the loss component.

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is considered impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been carried out without regarding these parameters as restricting technical features.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/FI 03/00867

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